PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method for preparing a Magnetic Recording Element and Coating Mixture therefor

We, RADIO CORPORATION OF AMERICA, a Corporation organized under the laws of the State of Delaware, United States of America, of 30, Rockefeller Plaza, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for preparing a magnetic recording element and to a coating mixture therefor.

A previously suggested method for preparing a magnetic recording element comprising magnetic particles in a cured polyurethane binder includes preparing a dispersion of magnetic particles in a nonaqueous liquid containing an isocyanate-terminated prepolymer; adding to the dispersion a nonpolymeric bifunctional compound in an amount insufficient to react with all of the free isocyanate groups of said prepolymer to produce a coating mixture; coating the mixture on a base, and then drying and curing the coating. During drying and curing, the isocyanate groups link to the bifunctional compound and to one another to produce a cured or "thermoset" binder.

Among the problems associated with this and similar methods are the problems that the coating mixture tends to gel, and that the coating mixture has a short pot life. Also, nodules sometimes appear at the surface of the cured magnetic coating. These problems are believed to result from premature curing of the coating mixture. In particular, it is believed that, upon contact with one another, the prepolymer reacts with reactive centres located in or on the magnetic particles forming agglomerates including more or less cured binder. The reactive centres may be, for example, reactive surface bonds of the magnetic material *per se*, or may be adsorbed chemicals, such as water, on the surface of the particles.

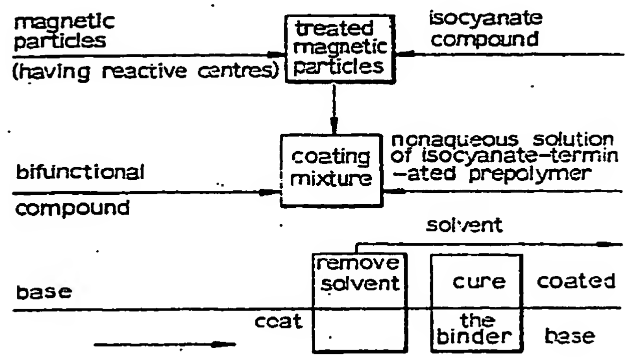
By rendering the reactive centres on the magnetic particles inactive, the magnetic particles are more easily dispersed in the coating mixture, the coating mixture has a longer pot life, and the coating mixture has a reduced tendency to gel. The remaining steps are completed in the usual way, to produce a coating having a smoother surface and improved magnetic properties compared to similar coatings produced with untreated magnetic particles.

The present invention accordingly provides a method of preparing a magnetic recording element by coating on a base a dispersion of magnetic particles in a nonaqueous liquid containing a isocyanate-terminated prepolymer and a nonpolymeric bifunctional compound in an amount insufficient to react with all of the free isocyanate groups in the prepolymer and then drying and curing the coating on the base, comprising contacting the magnetic particles, before mixing with the prepolymer and bifunctional compound, with an isocyanate compound which is liquid or in a liquid medium or a gas to form a reaction product between reactive centres on the magnetic particles and the isocyanate compound which is adherent to the surface of the magnetic particles.

The present invention also provides a coating mixture for preparing a magnetic recording element comprising the reaction product of magnetic particles having reeactive centres and a isocyanate compound, a non-aqueous liquid containing isocyanate-prepolymer and a nonpolymeric bifunctional compound, said bifunctional compound being present in an amount insufficient to react with all of the free isocyanate groups in the prepolymer.

[*Price 4s. 6d.*]

A simplified flow diagram of the method of preparing the magnetic recording element is as follows:



In the method of the flow diagram, the magnetic particles may be any of the usual magnetic particles used in magnetic recording elements. For example, one may use metallic particles, such as iron particles, or oxidic particles, such as gamma iron oxide, magnetite, zinc ferrous ferrite, or chromium dioxide. The preferred magnetic particles are of the oxidic type, are elongated or acicular in shape, and are preferably between 0.2 and 2.0 microns long, between 0.02 and 0.6 micron wide, and have an average length-to-width ratio between approximately 2 and 20, but usually approximately 6.

Any of a wide variety of isocyanate compounds may be used to treat the magnetic particles. The isocyanate compounds may be used as liquids, as gases, or as nonaqueous solutions. The preferred reactive isocyanate compounds are selected from the class consisting of aromatic and aliphatic diisocyanates. Some representative compounds which may be used are phenyl isocyanate, dodecyl isocyanate, tolylene diisocyanate, m-phenylene diisocyanate, 4 - chloro - 1, 3 - phenylene diisocyanate, 4,4′ - biphenylene diisocyanate, 1,5 - naphthalene diisocyanate, 1,6 - hexamethylene diisocyanate, 14 - cyclohexylene diisocyanate, and 1,5 tetrahydronaphthalene diisocyanate.

In general, the magnetic particles having reactive contents may be treated by contacting them with an isocyanate compound. The treatment may be carried out by contacting the particles in dry form with the isocyanate compound in gaseous form. Preferably, this gaseous treatment is carried out in a closed chamber in an atmosphere that is essentially saturated with the isocyanate compound, at elevated temperatures, preferably between 100 and 200° C, until the treatment is completed, which is usually of the order of approximately 1 hour.

The treatment may also be carried out by contacting the magnetic particles with a liquid isocyanate compound or with a more aqueous solution of an isocyanate compound. In either case, it is preferred to mill the magnetic particles in the liquid medium until the treatment is completed. The preferred method is to mill the magnetic particles in a nonaqueous solution of an isocyanate compound maintained between 15 and 30° C for between 1 and 4 hours. Milling is preferred because the surfaces of the particles intimately contact substantial amounts of the solution. Generally, the higher the temperature of the solution, the faster the reaction proceeds. However, too rapid a reaction rate results in agglomerates of the magnetic particles. It is preferred for the reaction to proceed at the fastest rate consistent with producing a uniform dispersion of treated particles in the solution. Milling is helpful in reducing the tendency of the particles to agglomerate at the faster reaction rate.

After the particles have been treated, the coating mixture is prepared. Where the treatment is carried out in a solution of an isocyanate compound or in a liquid isocyanate compound, the additional constituents (the prepolymer and the bifunctional compound) may be added to the dispersion of treated particles without drying the particles. Where the particles have been subjected to the gaseous treatment, they are first dispersed in a nonaqueous liquid such as methyl ethyl ketone and the additional constituents are added to this dispersion.

The coating mixture is prepared by adding to the dispersion of magnetic particles in the nonaqueous medium, a nonaqueous solution of an isocyanate-terminated prepolymer and then, subsequently adding a bifunctional compound. Generally, the prepolymer is prepared by reacting a molar excess of an organic diisocyanate with one or more polymeric organic compounds having a molecular weight of at least 750 and having two

terminal hydroxyl groups and selected from the group consisting of (1) polyalkylene-ether glycols, such as polytetramethyleneether glycol, polypropyleneether glycol and poly-1,2-butyleneether glycol, (2) polyalkylenearyleneether glycols, (3) polyalkylene-ether-thioether glycols, (4) polyalkylenearyleneether-thioether glycols, (5) linear, dihydroxy terminated polyesters, such as are prepared in a manner known to us by esterification of dihydric alcohols, such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butylene glycol with dibasic organic acids such as adipic acid, glutaric acid, suberic acid, sebacic acid and (6) linear, dihydroxy-terminated polyester amides.

Any of a wide variety of organic diisocyanates may be used in the foregoing reaction including aromatic, aliphatic, and cycloaliphatic diisocyanates, and combinations of these types. Representative compounds include tolylene diisocyanate, m-phenylene diisocyanate, 4 - chloro - 1, 3 - phenylene diisocyanate, 4,4′ - biphenylene diisocyanate, 1,5 - naphtalene diisocyanate, 1,6 - hexamethylene diisocyanate, 1,4 - cyclohexylene diisocyanate and 1,5 - tetrahydronaphthalene diisocyanate.

Any of a wide variety of bifunctional compounds may be used in preparing the coating mixture. The bifunctional compounds have at least two hydrogen atoms which are capable of reacting with isocyanates to form a polyurethane coating. Some suitable bifunctional compounds are water, ethylene glycol, hexamethylene glycol, monoethanolamine, m - phenylenediamine, 4,4′ - methylene dianiline and 4,4′ - methylene - bis-(2 - chloroaniline).

In preparing the coating mixture, it is preferred to mill the dispersion of magnetic particles with the isocyanate-terminated prepolymer. The milling may be continued between approximately 1 and 10 hours at temperatures between approximately 15 and 30° C. The bifunctional compound is added to the milled dispersion and the dispersion is remilled for a period of between 0.1 and 4 hours at room temperature to produce the coating mixture. The coating mixture is milled in a container which is closed from the atmosphere and particularly from water and water vapour, which has the effect of accelerating the curing of the mixture. The coating mixture may be stored for a substantial period of time in such a container which is closed from the atmosphere. It is preferred, however, to produce the magnetic coating as soon as possible after the coating mixture is prepared.

The coating is produced by any of the methods known in the art. As shown in the flow diagram, a base is coated with the coating mixture and then dried to remove the solvent from the coating and finally the binder is cured to produce the final product. The base is preferably an oriented polyethylene terephthalate film. Other suitable bases are made of paper, cellulose acetate, nylon, and oriented polyvinyl chloride. The base is typically 1.5 mils thick, although other thicknesses usually between 0.25 and 5.0 mils may be used. The film base may be of any convenient width for example, between 0.25 and 4.0 inches; and may be of any length usually thousands of feet.

The coating may be carried out by spraying, dipping, transfer roll coating, or gravure roll coating, but is preferably carried out by the process known as doctor blading. In the doctor blading process, the base passes under a doctor blade or knife which has a quantity of a coating mixture behind it. As the film base passes under the doctor blade, a thin coating is deposited on the base. The blade or knife is adjusted to apply a quantity of coating mixture to the surface of the base which will provide a dry coating between 0.1 and 2.0 mils thick; preferably 0.5 mil thick. After the coating mixture is applied, the coating passes through a magnetic field to orient the magnetic particles herein in a desired direction.

After orienting the magnetic particles, the coating is dried in a dryer by removing the solvent, therefrom. The dry structure is then heated for a short period. The heating is carried out in a curing region in a separate oven or near the exit end of the drying oven. The heating is finally conducted at approximately 100 to 130° C for approximately 1 to 30 minutes. The final heating after the solvent is removed solidifies the coating sufficiently to permit the coated base to be wound on a take-up roller without sticking or blocking. Following this heating, the coated base is cooled and then wound on a take-up roll. At this stage, the coating is partially cured. The cure is completed by storing the wound roll for periods of one hour to several days at temperatures between approximately 40 and 120° C. During which period the cross linking reaction is completed. The coated base may now be slit to any desired width.

The following examples illustrate specifically several methods for practicing the invention:

Example 1—A mixture of 584 grams of acicular gamma iron oxide particles, 660 grams methyl ethyl ketone, and 54 grams tolylene diisocyanate was milled for approximately 3 hours at approximately room temperature. To this mixture were added 216

grams of an isocyanate-terminated prepolymer formed by the reeaction of tolylene diisocyanate with poly - (1,4 - butanediol), 100 grams of methyl ethyl ketone and 23 grams lecithin. The mixture was milled for another ten hours at room temperature. To the slurry thus formed, 54 grams of 4,4′ - methylene - bis - (2 chloroaniline) and 100 grams of methyl ethyl ketone were added and the milling was continued for two hours at room temperature. The resulting mixture was coated on a polyester film and the coated structure was heated to 120° C. for ten minutes. The magnetic tape made in this manner exhibited a surface smoothness of 6 microinches (root mean square), a retentivity B_r of 920 gauss, and a B_rB_{1000} of 0.80. A tape made in an identical fashion but not including the tolylene diisocyanate during the initial milling exhibited a surface smoothness of 16 microinches (root mean square), a retentivity of 780 gauss, and a B_rB_{1000} of 0.74.

Example 2—A mixture of 24 grams of acicular zinc ferrous ferrite particles, 45 grams of methyl ethyl ketone, and 2.0 grams of tolylene diisocyanate was milled for approximately three hours at approximately 15° C. To this mixture were added 6.6 grams of an isocyanate - terminated prepolymer formed by the reaction of tolylene diisocyanate with poly - 1(4 - butanediol), 12 grams of methyl ethyl ketone, 0.5 gram of a dispersant material, and 2.0 grams of 4,4′ methylene - bis - (2 - chloroaniline) and milling was continued for approximately four hours at about 15° C. The resulting mixture was coated on a polyester film and the coated structure was heated to approximately 100° C for approximately 15 minutes. The magnetic tape made in this manner exhibited a surface smoothness of 8 microinches (root mean square), a retentivity of 1050 gauss and a B_r/B_{1000} of 7.78. A tape made in an identical manner, but omitting the tolylene diisocyanate in the initial milling, had a surface smoothness of 16 microinches (root mean square), a retentivity of 900 gauss, and B_r/B_{1000} of 0.74.

Example 3—A mixture of 26 grams chromium dioxide particles, which have been surface treated with a Werner-type complex compound of chromium cations and stearic acid, 24 grams methyl ethyl ketone, and 2.0 grams tolylene diisocyanate was milled for approximately two hours at room temperature. To this mixture were added 7.0 grams of a bifunctional isocyanate terminated prepolymer formed by the reaction of tolylene diisocyanate with poly - (1,4 - butanediol), 7.0 grams of methyl ethyl ketone and 1.7 gram of 4,4′ - methylene - bis - (2 - chloroaniline) and milling was continued for about four hours at approximately 20°C. The resulting mixture was coated on a polyester film and the coated structure was heated at approximately 100° C. for approximately 15 minutes. The magnetic recording element made in this manner exhibited a surface smoothness of 8 microinches (root mean square), a retentivity of 1250 gauss, and a ratio of B_r/B_{1000} of 0.87. A magnetic recording element made in an identical manner but omitting the tolylene diisocyanate in the initial milling, had a surface smoothness of 16 microinches (root mean square), a retentivity of 960 gauss, and a B_r/B_{1000} of 0.83.

Example 4—A vessel containing 50 grams of acicular gamma iron oxide particles was evacuated to a pressure of 0.5 mm. of mercury and heated to a temperature of approximately 140° C. The vessel was closed from the vacuum system and approximately 1.8 gram of phenyl isocyanate was introduced into the vessel, where it evaporated, producing a substantially saturated atmosphere. The vessel, still closed from the vacuum system, was heated to approximately 160° C for approximately three hours. The vessel was then evacuated to a pressure of 0.5 mm. of mercury at 160° C. for one hour to remove the isocyanate compound. Thereafter, the vessel was allowed to cool to room temperature and the treated iron oxide removed. The treated gamma iron oxide particles thus obtained were hydrophobic and oleophilic. A mixture of 25 grams of the treated gamma iron oxide particles, 32 grams of methyl ethyl keton, 1.0 gram of lecithin, and 11 grams of an isocyanate-terminated prepolymer formed by the reaction of tolylene diisocyanate with poly - (1,4 - butanediol) was milled for approximately 5.5 hours. After this period, 3.6 grams of a 33.% (by weight) solution of 4,4′ - methylene-bis - (2 - chloroaniline) in methyl ethyl ketone were added to the mixture and milling was continued for another 30 minutes. The resulting mixture was coated on a polyester film and heated to approximately 120° C. for approximately ten minutes. The recording element made in this fashion had a retentivity B_r of approximately 860 gauss, a surface smoothness of 10 microinches (RMS), and a B_r/B_{1000} of 0.79. A recording element made in an essentially identical manner, but substituting an untreated gamma iron oxide for the treated iron oxide, had a surface smoothness of 16 microinches (RMS), a retentivity of approximately 780 gauss, and a B_r/B_{1000} of approximately 0.74.

WHAT WE CLAIM IS:—

1. A method of preparing a magnetic recording element by coating on a base a dispersion of magnetic particles in a non-aqueous liquid containing a isocyanate-ter-

minated prepolymer and a nonpolymeric bifunctional compound in an amount insufficient to react with all of the free isocyanate groups in the prepolymer and then drying and curing the coating on the base, comprising contacting the magnetic particles, before mixing with the prepolymer and bifunctional compound, with an isocyanate compound which is liquid or in a liquid medium or a gas to form a reaction product between reactive centres on the magnetic particles and the isocyanate compound which is adherent to the surface of the magnetic particles.

2. A method according to Claim 1 wherein said reactive centres arise from water absorbed on the surface of the magnetic particles.

3. A method according to Claim 1 wherein said isocyanate compound is either an aromatic or aliphatic isocyanate compound.

4. A method according to Claim 1 wherein said magnetic particles are either gamma iron oxide, zinc ferrous ferrite or chromium dioxide.

5. A method according to Claim 1 wherein the magnetic particles are contacted with a nonaqueous solution of the isocyanate compound.

6. A method according to Claim 5 wherein the mixture of magnetic particles and solution of isocyanate compound is milled between approximately 15—30°, to provide an intimate contact between the surface of the particles and the solution.

7. A method according to Claim 1 wherein treatment with a gaseous isocyanate compound is carried out in a closed chamber in an atmosphere that is essentially saturated with the isocyanate compound, at elevated temperatures between 100—200°C.

8. A method of making a magnetic recording element substantially as hereinbefore described, with reference to any one of Examples 1—4.

9. A magnetic recording element when made by a method according to any one of the preceding claims.

10. A coating mixture for preparing a magnetic recording element comprising the reaction product of magnetic particles having the reactive centres and a isocyanate compound, a non-aqueous liquid containing isocyanate-prepolymer and a nonpolymeric bifunctional compound, said bifunctional compound being present in an amount insufficient to react with all of the free isocyanate groups in the prepolymer.

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